Conformational Analysis of Organic Carbonyl Compounds. Part 9.[1] 2-Formyl-, 2-Acetyl-, and 2-(p-Methoxybenzoyl)-indene

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The conformational behaviour of 2-acylindenes has been examined in order to compare the results with those previously obtained for the acyl derivatives of benzo-condensed five-membered heterocycles and, from a more general point of view, with those of α,β-unsaturated carbonyl compounds. Experimentally, the problem was tackled with the LIS (lanthanide-induced shift) simulation method for ^1H and ^{13}C magnetic resonances and with the NOE (nuclear Overhauser effect) difference spectra on ^1H. *Ab initio* MO calculations were performed on carbonyl derivatives of cyclopentadiene, chosen as model compounds. The experimental results, qualitatively from NOE measurements and more quantitatively from LIS simulation, indicate that these molecules adopt a preferential *s-trans* orientation for the C=O bond and the internal double bond of the indene ring, planar for the formyl and acetyl derivatives. In the *p*-anisoyl derivative the phenyl and indene rings are twisted (the former to a greater extent) with respect to the carbonyl plane. The same situation is provided by the theoretical treatment of the corresponding cyclopentadiene derivatives.

The conformational behaviour of 2- and 3-acyl derivatives of five-membered heterocycles, mainly furan, thiophene, and their benzo-condensed forms, has been extensively studied [1–9] and the preferred orientation of the carbonyl group relative to the heterocyclic ring derived. In the stable conformation of the 2-formyl and 2-acetyl derivatives the carbonyl group and the heterocyclic ring are coplanar. For the 2-benzoyl and 2-*p*-methoxybenzoyl derivatives conformational behaviour close to that found for the corresponding formyl and acetyl derivatives was observed,[1,2,4,9] the preferred relative orientation of the carbonyl oxygen and of the heteroatom being of the same type, but the carbonyl group is not coplanar with the attached rings.

The conformational situation of acylindenes has been less studied but, on the other hand, it can be interestingly compared with that of the acyl derivatives of benzo[b]furan and benzo[b]thiophene to check the effect of the replacement of O and S by a CH_2 group on the conformational behaviour of the carbonyl group, especially when present in position 2.

For acyclic α,β-unsaturated carbonyl derivatives, which are structurally related to the compounds here examined, the following conclusions were obtained. In acrolein the stable conformers are planar and the *s-trans* form has been found both experimentally [10] and theoretically [11] to be the more stable. The *s-trans* conformation is preferred even when alkyl groups are *cis* [12–15] and geminal [13–15] to the formyl group. The *s-trans* form has been found [12,14,16] to be more stable for methyl vinyl ketone, the acetyl group being [12] slightly twisted relative to the adjacent double bond. The presence of a methyl substituent *cis* to the acetyl group makes the *s-cis* form more stable,[12,14,15,17] The planarity of the conformers of these compounds is not unequivocally stressed.[12–14,17] The conformational situation for benzoyl derivatives, relatively less studied than compounds containing the formyl and acetyl groups, appeared to indicate that the *s-cis* form is preferred [15] when a *cis*-methyl group is present, while a geminal methyl group causes severe twist of the C=C and C=O planes (60—70°).

In view of these experimental peculiarities concerning acyl derivatives of five-membered heterocycles and open-chain α,β-unsaturated ketones and aldehydes, we have undertaken a study of the conformational properties of 2-acylindenes both with experimental methods and with *ab initio* MO calculations on the corresponding derivatives of cyclopentadiene, chosen as model compounds.

Results and Discussion

The conformational study was carried out on derivatives (1)—(3) and the experimental approach was based on ^1H and ^{13}C n.m.r. spectroscopy. The lanthanide-induced shift (LIS) method [18] and nuclear Overhauser effect (NOE) measurements were employed. The ^1H and ^{13}C chemical shifts utilized in LIS simulation are reported in Table 1. Complete analysis of the ^1H multiplets was performed with the MIMER program.[19] In the

(1)

(2)

(3)
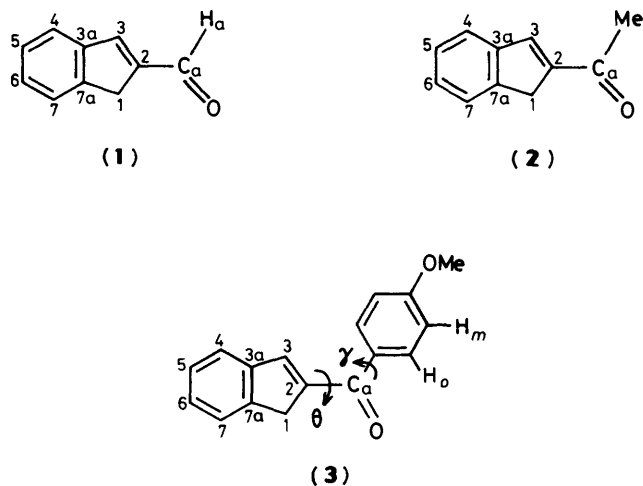
^1H spectrum of compound (1) in [^2H]chloroform and [$^2H_6$]acetone solutions the long-range $^4J(H_a\text{-}H_3)$ coupling was not observed and, from the line width, this constant should be <0.1 Hz. Since this ^4J coupling constant in formyl derivatives [20,21] of benzene and of five-membered heterocycles is larger (0.4—0.5 Hz) for a *trans* arrangement of coupled protons and nearly zero for their *cis* orientation, the *s-trans* form of compound (1) should predominate in both solvents.

LIS Measurements.—Quantitative results for the conformational behaviour of these molecules were obtained from simulation of the experimental LIS values. Observed LIS values (ΔM), measured on the same sample for ^1H and ^{13}C resonances, obtained in presence of Yb(fod)$_3$, diamagnetic shifts for complex

Table 1. ¹H and ¹³C n.m.r. chemical shifts (δ values) for compounds (1)—(3) recorded in [²H]chloroform solution. ΔM are the LIS values and refer to Yb(fod)₃, $(\Delta M - \Delta D)$ are corrected for the complexation shift[22] in presence of La(fod)₃

	(1)			(2)			(3)		
	δ	ΔM^a	$(\Delta M - \Delta D^b)$	δ	ΔM^c	$(\Delta M - \Delta D^d)$	δ	ΔM^e	$(\Delta M - \Delta D^f)$
1-H	3.65	29.03		3.60	28.44		3.85	26.82	
3-H	7.71	17.45		7.56	21.28		7.43	21.11	
2'-H							7.84	30.05	
3'-H							6.96	6.01	
Other ¹H resonances	9.77^g	67.50		2.41^h	34.10				
C-1	35.60	31.26	31.26	37.50	32.87	32.87	38.92	33.92	33.92
C-2	147.20	45.22	46.92	146.41	51.93	53.37	145.51	57.41	58.55
C-3	147.63	28.07	20.55	141.03	30.36	22.95	142.18	31.40	24.38
C-4	124.29	8.64	7.61	123.82	8.43	7.31	123.73	7.70	7.70
C-5	127.22	5.85	5.30	127.01	5.04	5.04	127.00	4.06	4.06
C-6	128.93	7.09	5.85	128.17	5.73	3.78	127.89	4.24	2.79
C-7	124.87	8.33	8.33	124.56	6.34	6.34	124.48	4.09	4.09
C-3a	142.34	13.26	13.26	142.90	13.01	13.86	143.21	12.77	13.69
C-7a	145.15	16.23	14.67	145.07	15.38	13.78	144.90	13.84	11.83
C=O	188.16	124.25	118.05	195.42	122.54	113.96	191.54	122.46	118.41
C-1'							131.65	53.50	56.10
C-2'							131.26	31.34	28.70
C-3'							113.69	12.00	12.00
C-4'							162.97	10.77	8.83

^{a} [S] 0.33M; χ 0.042, 0.063, 0.0875, 0.1035. ^{b} [S] 0.30M; χ 0.028, 0.049, 0.096, 0.121. ^{c} [S] 0.264M; χ 0.038, 0.062, 0.087, 0.109. ^{d} [S] 0.286M; χ 0.043, 0.071, 0.092, 0.12. ^{e} [S] 0.31M; χ 0.042, 0.063, 0.082, 0.103. ^{f} [S] 0.294 M; χ 0.036, 0.0656, 0.0987, 0.1187. ^{g} Formyl proton. ^{h} Methyl protons.

Table 2. Results of LIS simulation: molecular geometry parameters for the complexes^a and conformational properties of derivatives (1)—(3)

								Conformational angles^b (°)	
Compound	$R_{cryst.}$	Sum-dif.	R(Å)	φ	ψ	f	Population endo	θ	γ
(1)	0.014	0.607	2.60	55°	140°	2 836.38	0	0	
(2)	0.021	0.856	2.95	55°	150°	3 670.09	20	0	
(3)	0.029	1.092	2.90	55°	160°	3 812.65	45	10	30

^{a} For symbols see ref. 22. ^{b} Error in angles estimated as ±10°.

formation[22] (ΔD) on ¹³C shifts using La(fod)₃, and pseudocontact shifts $(\Delta M - \Delta D)$ are reported in Table 1. The method employed was derived from literature sources[22] and also described in our previous work.[9] The molecular geometry employed for compounds (1)—(3) was constructed from standard[23] bond distances and angles for the indene ring, while for the carbonyl group the geometrical parameters were taken from the results of geometry relaxation from *ab initio* MO calculations (3-21G basis set) of the corresponding cyclopentadiene derivatives. The LIRAS-3 computer program[22] was employed in the 'four-sites' axially symmetric complexation model. The conformational results obtained from LIS simulation are reported in Table 2, and the symbols have their usual meaning.[22] The conformation corresponding to γ 0 and θ 0° is that depicted in the formulae. The best agreement between experimental and calculated LIS values $(R_{cryst.})$ was obtained for amounts near 100% of the conformation reported in Table 2. Better agreement was not reached by weight-averaging non-planar conformations.

The three compounds examined show a clear preference for the *s-trans* orientation. Compounds (1) and (2) are nearly planar while for compound (3) a twist from the carbonyl plane is found for the phenyl and indenyl ring, higher for the former.

NOE Measurements.—The preferred conformation for compounds (1)—(3) was also confirmed by ¹H NOE difference spectra. Measurements were carried out on degassed chloro-

form solutions. The protons irradiated and observed are shown in Table 3, where the NOE difference values are reported.

On irradiating H-3, besides the enhancement observed for H_a (1), CH₃ (2), and *o*-H (3), a positive NOE should also be generated on H-4 and the same should occur on H-7 when 1-H₂ is irradiated. We nevertheless confined the analysis of the enhancements observed to those protons reported in Table 3 and ignored effects from other protons or groups of protons. As a consequence, only approximate indications on the conformational situation of these molecules could be derived.

The results reported in Table 3 show that for compounds (1) and (2) the highest enhancements are observed when H-3 is irradiated and H_a or CH₃ is observed in that order. The same is true when the irradiated and observed protons are interchanged. These results should approximately indicate that H_a or the Me group [(1) and (2)] are closer to the 3-H than to the 1-H₂ group, and this occurs also in compound (3) when 3-H and *o*-H are involved.

A test of the reliability of this conclusion has been carried out, for compounds (1) and (2), on the basis of internuclear distances, by adopting an approximate formulism derived from the NOE general equation for multispin systems.[24]

For compound (3) no attempt was made to relate experimental NOE values to internuclear distances through theoretical expressions, because of the complexity of the molecule. It was nevertheless seen that small but still measurable enhancements are obtained by irradiating 3- or *o*-H

and observing o- or 3-H. Furthermore, when 3-H is saturated, a negative NOE is observed for the protons in the *meta* position of the phenyl ring (relative NOE −0.02). This seems characteristic of an arrangement of 3-, o-, and m-H approaching that of

the 'linear three-spin system' (or, more properly, of the 'acute case' arrangement[24]), when one of the external protons is irradiated. These results are in better agreement with the *s-trans* conformation for compound (3).

MO Ab-initio Calculations.—The relative stability of the conformers of α,β-unsaturated carbonyl compounds was predicted with *ab-initio* MO calculations. In acrolein,[25] the *s-trans* is more stable than the *s-cis* form at the 6-31G* level with the geometry optimized at the 3-21G level (6-31G*//3-21G), in agreement with experimental observations, while at the 3-21G//3-21G level the two orientations have[25] the same energy content. For formyl derivatives of furan and thiophene, calculations at the 3-21G//3-21G level provide,[3,26] as a general rule, the correct order of stability of the X,O-*cis/trans* conformers, whereas this is not obtained with the minimal STO-3G basis set.

A test of the relative conformer stability in acyl derivatives of indene from *ab initio* MO methods in basis sets larger than the minimal STO-3G one is prohibitive owing to molecular size, hence we chose model compounds (4) and assumed that their conformational behaviour should be not too dissimilar from that of the compounds examined from the experimental point of view.

A preliminary test carried out on compounds (1) and (4a), by employing the Gaussian-82 program[27] at the 3-21G level with standard molecular geometries, showed that the *s-trans* form is

Table 3. Results of NOE difference measurements in compounds (1)—(3) and relaxation times T_1 for compounds (1) and (2)

| Compound | Proton(s) observed | Proton(s) irradiated | | | T_1/s |
		{H_a}	{3-H}	{1-H_2}	
(1)	H_a		0.223	0.025	9.40
	3-H	0.153		0.013	9.75
	1-H_2	0.004	0.019		4.27

| Compound | Proton(s) observed | Proton(s) irradiated | | | |
		{CH_3}	{3-H}	{1-H_2}	
(2)	CH_3		0.049	0.00	6.07
	3-H	0.183		0.029	13.01
	1-H_2	0.00	0.015		3.52

| Compound | Proton(s) observed | Proton(s) irradiated | | | |
		{o-H}	{3-H}	{1-H_2}	
(3)	o-H		0.11	0.00	
	3-H	0.018		0.015	
	1-H_2	0.00	0.00		

Table 4. Results of geometry relaxation at the 3-21G//3-21G level in compounds (4a—c) and in acetophenone. The geometry of the cyclopentadiene ring is averaged over the compounds examined
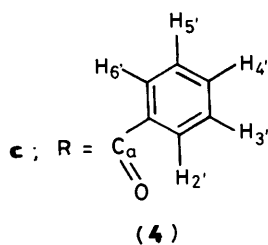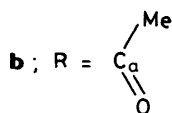
| | (4a) | | (4b) | | (4c) | | Acetophenone |
	s-cis	*s-trans*	*s-cis*	*s-trans*	*s-cis*	*s-trans*	
C(2)–C$_a$	1.457	1.453	1.470	1.466	1.476	1.470	
C$_a$–O	1.215	1.214	1.217	1.217			1.215
C$_a$–H	1.086	1.087					
C$_a$–C(H$_3$)			1.514	1.514			1.514
C–H(CH$_3$)			1.083	1.083			1.083
C(2)–C$_a$–O	124.5	124.3	121.4	120.6			
H–C$_a$–O	120.9	121.2					
C(3)–C(2)–C$_a$	124.9	126.8	123.6	129.5	122.0	130.5	
C–C$_a$–O			122.1	122.2			121.7
C(3)–C(2)–C$_a$–O	0.0	180.0	0.0	180.0	21.1	200.6	
C(6')–C(1')–C$_a$–O					40.3	32.1	−0.0$_2$

Cyclopentadiene ring

C(1)–C(5)	1.515 ± 0.001
C(1)–C(2)	1.515 ± 0.003
C(2)–C(3)	1.334$_5$ ± 0.000$_1$
C(3)–C(4)	1.475 ± 0.001
C(4)–C(5)	1.332 ± 0.000$_4$
C(1)–H(1)	1.086$_1$ ± 0.000$_5$
C(3)–H(3)	1.069$_3$ ± 0.000$_6$
C(4)–H(4)	1.068$_3$ ± 0.000$_8$
C(5)–H(5)	1.068$_8$ ± 0.000$_5$
C(1)–C(5)–C(4)	110.0$_1$ ± 0.0$_6$
C(2)–C(3)–C(4)	109.5 ± 0.1
C(3)–C(4)–C(5)	108.9$_6$ ± 0.0$_3$
H(3)–C(3)–C(2)	125.6 ± 0.7
H(4)–C(4)–C(3)	124.3 ± 0.1
H(5)–C(5)–C(1)	123.4 ± 0.2

Benzoyl ring

C(1')–C(2')	1.386
C(1')–C(6')	1.388
C(1')–C$_a$	1.494
C(2')–C(3')	1.384
C(3')–C(4')	1.383
C(4')–C(5')	1.386
C(5')–C(6')	1.379
C(2')–H(2')	1.071
C(3')–H(3')	1.072
C(4')–H(4')	1.072
C(5')–H(5')	1.072
C(6')–H(6')	1.070
C(1')–C$_a$–O	120.5
C(2')–C(3')–C(4')	120.0
C(3')–C(4')–C(5')	120.0
C$_a$–C(1')–C(6')	117.2
C(1')–C(2')–H(2')	120.6
C(1')–C(6')–H(6')	118.3
C(2')–C(3')–H(3')	119.9
C(3')–C(4')–H(4')	120.0
C(4')–C(5')–H(5')	120.1

* Dependent parameter.

Table 5. Relative energy (kJ mol⁻¹) and dipole moments (10^{-30} C m) of the stable conformations of compounds (4a—c) (calculated at the 3-21G//3-21G level)

Compound		ΔE	μ
(4a)	s-cis	5.3024	12.43
	s-trans	0	11.40
(4b)	s-cis	3.2595	12.36
	s-trans	0	10.58
(4c)	s-cis	11.2418	12.15
	s-trans	0	10.63

the more stable and the energy difference between conformers in the two derivatives is quite small [(1), ΔE 4.42; (4a), ΔE 4.48 kJ mol⁻¹]. Calculations on molecules (4a—c) were then performed at the 3-21G level, allowing for geometry relaxation. For

(4)

derivatives (4a and b) full geometry relaxation was allowed. For derivative (4c) the geometry of the cyclopentadiene ring optimized in (4a and b) and that of the phenyl ring optimized in acetophenone were kept constant, while the parameters relative to the carbonyl group (Table 4) were allowed to relax. The exocyclic bond-angles made by the C–C(O) bond with the cyclopentadiene ring in the two conformers of each compound were found to be significantly different. The exocyclic C(2)–C(O) bond is slightly shorter in the s-trans conformer, which should indicate a higher π-conjugation between the C=O and the adjacent C=C bond of the ring in the more stable form. For derivatives (4a and b) the stable conformations were found planar, while those of compound (4c) show both rings twisted from the carbonyl plane, the phenyl ring deviating more. The dihedral angles between the C=O plane and the cyclopentadiene ring in the two conformers of compound (4c) are very close [compare the values of C(3)–C(2)–C_a–O in Table 4] while a larger twist is found for the one relative to the phenyl ring in the s-cis than in the s-trans conformer. This result could indicate that steric interactions involving the phenyl ring are stronger with the methylene protons of the cyclopentadiene ring than with 3-H. In consequence the s-trans form of compound (4c) should be more stable for steric reasons as well.

From the energy differences between conformers (Table 5), assumed to be close to free-energy values, the amount of s-trans conformer is estimated 89, 80, and 99% in derivatives (4a—c).

Although these estimates refer to model compounds in an ideal gas phase and the 3-21G basis set probably underestimates the difference in stability of these molecules, the prediction of the prevailing presence of the s-trans conformer should also apply to the compounds (1)—(3).

Calculated dipole moments, reported in Table 5, show that the s-trans form is the less polar one. For compounds (1)—(3) experimental dipole moments are not known, but if they behave like the model compounds (4a—c), electrostatic factors also favour the presence of the s-trans conformer, at least in solutions with low permittivity.

Conclusions.—The NOE and LIS measurements agree in showing that derivatives (1)—(3) prefer the s-trans conformation. The coplanarity of the indene ring and carbonyl group in the formyl and acetyl derivatives and the twist of the rings, larger for the phenyl ring, found in compound (3), show that the conformational trends[4–9] for the corresponding derivatives of furan and thiophene are also present in these molecules. Theoretical calculations on the model compounds (4a—c) predict conformational trends close to those observed in derivatives (1)—(3). The all-planar s-trans conformation for compound (3) should be sterically unfavourable and the rings should rotate from coplanarity: as occurs for benzoyl derivatives[1,2,4,9] of five-membered heterocycles, the higher twist is found for the ring with higher π-electron delocalization. The twist of the indene ring is small and not as severe as that reported[15] for the C=C and C=O planes in α,β-unsaturated ketones $R^1R^2C=CR^3COPh$, when R^3 is a methyl group.

Experimental

Compounds.—Indene-2-carbaldehyde (1) was obtained in 50% yield from indene-2-carbonyl chloride[28] by reduction with bis(triphenylphosphine)copper(I) tetrahydroborate,[29] sublimation at 45 °C and 0.2 mmHg and crystallization from cyclohexane, m.p. 48—50 °C (lit.,[30] 49—50.5 °C). 2-Acetylindene (2) was obtained in 32% yield from indene-2-carbonyl chloride[28] by the diethyl acylmalonate method of ketone synthesis,[31] sublimation at 55 °C and 0.1 mmHg, and crystallization from hexane, m.p. 60—61 °C (lit.,[28,32] 59—60 °C).

2-(p-*Methoxybenzoyl*)*indene* (3). A solution of indene-2-carbonyl chloride[28] (3.57 g, 20 mmol) and anisole (2.49 g, 23 mmol) in dry CS_2 (42 ml) was cooled at 10 °C. Anhydrous $AlCl_3$ powder (2.93 g, 22 mmol) was added and the resultant orange precipitate was stirred at room temperature for 48 h. Dilute HCl (2M; 20 ml) was added to the mixture, allowing the temperature to rise to 40 °C. After cooling, the organic material was extracted with $CHCl_3$ and the latter washed twice with dilute NaOH and dried ($MgSO_4$). Solvent evaporation and crystallization of the residue from ligroin (b.p. 90—120 °C) yielded a product (4.0 g, 80%), m.p. 141—143 °C. Further crystallization and sublimation (130 °C and 0.1 mmHg) did not raise the m.p. (Found: C, 81.0; H, 5.6. Calc. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6%).

N.m.r. Measurements.—The spectra were recorded at 200.058 MHz for ¹H and 53.3088 MHz for ¹³C by employing a Varian XL-200 spectrometer. [²H]Chloroform solutions (ca. 0.3M) were employed and ¹³C proton-decoupled spectra were obtained from natural-abundance samples. Tetramethylsilane was added to the solutions as an internal standard. The shift reagent employed was Yb(fod)₃ dried *in vacuo* over phosphorus pentaoxide, added in known amounts (the molar ratios χ between shift reagent and substrate concentrations are reported in the footnotes to Table 1) to [²H]chloroform solutions of the substrate examined. The correlation coefficients for the plots relating chemical shifts to the lanthanide:substrate ratio were

always found to be $\geqslant 0.999$ and the intercepts were identical to those of the unshifted spectra.

^{1}H T_1 measurements were made at room temperature (23 °C) for compounds (1) and (2) with standard inversion–recovery sequences (180°–τ–90°–RD) by employing 12 random values of τ. Least-squares fits were employed to determine the T_1 values.

Nuclear Overhauser effect (NOE) measurements were made on the same sample used for ^{1}H T_1 determinations. Accurately degassed samples were prepared from [^{2}H]chloroform solutions (*ca.* 0.3M). NOE difference spectra were obtained on a Bruker WP-80 spectrometer (80 MHz) by acquiring alternate groups of eight transients for each irradiating frequency, preceded by four dummy scans and with each transient separated by a relaxation delay of 5 s. The flip-angle employed was 20° with a low-power decoupler setting (55L). This cycle was repeated 32 times or more by using sweep-widths of 1 200 Hz and 8 K data points. Spectra with NOE and reference spectra were acquired alternately in order to minimize long-term drifts. Percentage enhancement was determined by integration of NOE difference spectra relative to reference spectra.

Calculations were performed on CRAY-X-MP12 and VAX-750 computers.

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